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Transmission Electron Microscope Study of Neutron Irradiation-induced Defects in Silicon

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Commercial Czochralski-grown silicon (Cz-Si) and float-zone silicon(Fz-Si) wafers were irradiated with fission neutrons at various fluences from 10^{19} to 10^{22} n/cm^2 at temperatures ranging from 473K to 1043K. The irradiation induced defect structures were examined by transmission electron microscopy and ultra high voltage electron microscopy, which were compared with Marlowe code computer simulation results. It was concluded that the vacancy-type damage structure formed at 473K were initiated from collapse of vacancy-rich regions of cascades, while interstitial type defect clusters formed by irradiation above 673K were associated with interstitial oxygen atoms and free interstitials which diffused out of the cascades. Complex defect structures were identified to consist of {113} and {111} planar faults by the parallel beam illumination diffraction analysis.

KEYWORDS: silicon, neutron irradiation-induced defect, transmission electron microscopy, ultra high voltage electron microscopy, cascade structure, planar fault

1. Introduction

Extensive irradiation studies have been carried out so far in order to examine behavior of intrinsic point defects and impurity-point defect complexes of silicon by introduction of a large number of radiation-induced vacancy-interstitial pairs. Nowadays, silicon is the most popular electronic material, and its application is increasingly extended. With recent development of very large scale integrated circuits of semiconductor devices, considerable effort has been directed toward complete annihilation of the lattice defects in the device construction regions of silicon wafers. In addition, the device application under severer environmental conditions has been expanded, e.g. in outer space where the devices are exposed to cosmic rays. In this case, the collision probability may not be high, but the momentum of an incident particle is so large that the irradiation effect is unable to ignore. In this study, we have irradiated silicon wafers heavily with fission neutrons using reactors of JMTR and JOYO, and some preliminary results examined by transmission electron microscopy are reported.

2. Experimental

3mm disc specimens were cut from commercial float-zone(Fz) silicon and Czochralski-grown(Cz) silicon wafers with <111> and <011> orientations by an ultrasonic drill. They were mounted in capsules for neutron irradiation prepared by Ooarai Branch of the Institute for Materials Research of Tohoku University, and irradiated by reactors of a light-water type JMTR and a fast breeder type JOYO. The neutron fluences were from 10^{19} and 10^{22}n/cm^2 and the irradiation temperatures were ranged from 473K to 1043K. The irradiated specimens were kept at storage facilities until radio activities of the capsules were decayed. The recovered specimens were chemically thinned in a mixed solution of hydrofluoric acid and nitric acid for transmission electron microscopy. They were observed using a transmission electron microscope of JEM-200CX which was operated at 160kV to avoid an extra electron irradiation effect. Some specimens were then examined by a high voltage electron microscope of Osaka University, HU-2000, which was operated at 2MV.

For ease of comparison with experiments, computer simulation of neutron irradiation effect was also done based on the Marlowe code.[1]

3. Results

(1) JMTR, 473K, 2.5x10^{19}n/cm^2

It appeared from conventional transmission electron microscopy that neutron irradiation-induced defects were not formed. However, weak beam dark field micrographs showed fine defect clusters of blight dotted contrast with a size of several nanometers which were distributed uniformly in the specimen as shown in Fig.1. The observed defect densities were the order of 10^{16}/cc, the value of which is two orders in magnitude smaller than the total cascade density computed from the product of fluences, reaction cross section for 1.5MeV neutrons(3 barn[2]) and the density of

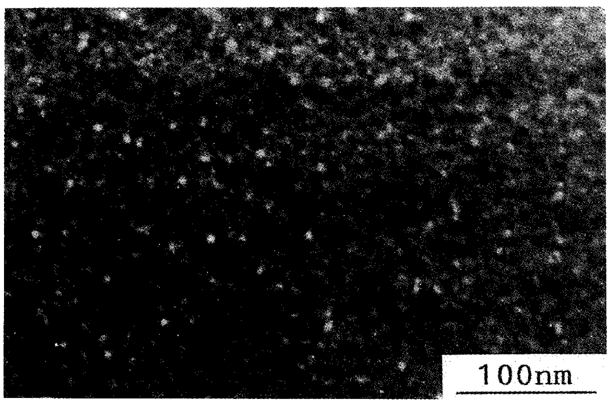


Fig.1 Weak beam electron micrograph of vacancy-type defect clusters of Cz-Si irradiated at 473K with fission neutrons at the fluence of 2.5x10^{19}n/cm^2. (Improved temperature control)

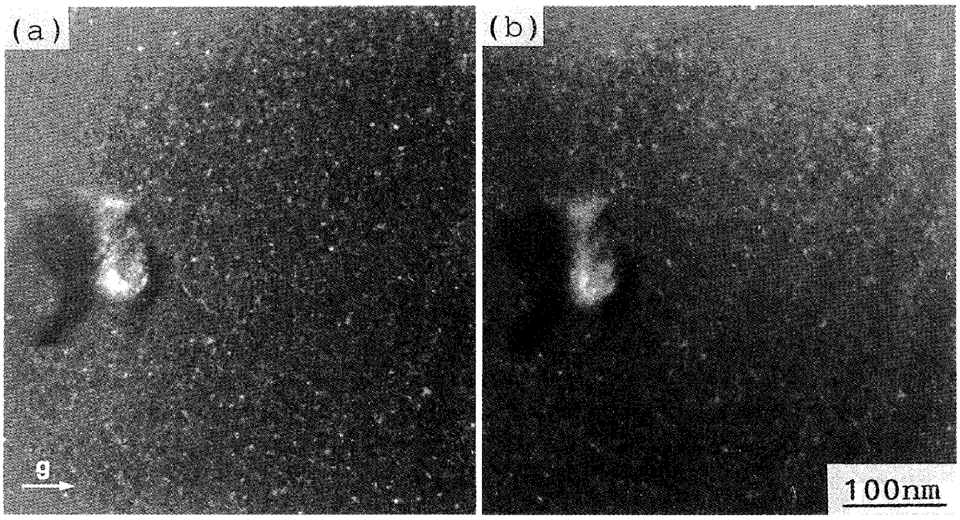


Fig.2 Determination of the nature of microdefects of Fz-Si irradiated with improved temperature control at 473K with fission neutrons of JMTR at the fluence of $2.5x10^{19}n/cm^2$ by the 2·1/2D method. (a) in focus, and (b) over focus pair.

atoms($5x10^{22}/cm^3$). No marked difference in damage structures was observed between Fz–Si and Cz–Si. In order to determine the nature of the defects, the 2·1/2D method was used. An example is shown in Fig.2, and it was found that the nature is vacancy type.

(2)JMTR, 673K, $9.2-9.6x10^{19}n/cm^2$

As already pointed out by Kiritani *et al.*[2]) temperature change due to nuclear power fluctuation by the start up and shut down of the reactor has direct effects on the nucleation of irradiation–induced defects. Accordingly, two different irradiation temperature control modes were used in the present work. The first was "improved temperature control irradiation", and the second is "conventional temperature control irradiation". In the former, irradiation was performed only under the constant temperature of 673K with the fluence of $9.6x10^{19}n/cm^2$, and in the latter, irradiation was carried out continuously with the fluence of $9.2x10^{19}n/cm^2$ from the start up to shut down of the reactor. It was found that colonies of several hundred nanometers with a high density of {113} interstitial type defect clusters were formed in Cz–Si as shown in Fig.3, while defect clusters of about ten nanometers were observed in Fz–Si. The densities of defect clusters of Cz–Si and Fz–Si evaluated from micrographs are shown in Table 1. It is found that the defect density of "conventional temperature control irradiation" is about twice of that of "improved temperature control irradiation", indicating that the nucleation is more enhanced at temperatures lower than 673K.

In-situ observation using a high voltage electron microscope (HVEM) was also carried out to identify the neutron irradiation–induced secondary defects. Our previous HVEM experiments have indicated that interstitial type {113} dislocation loops were formed uniformly in Cz–Si specimens except for denuded zones near the specimen surfaces immediately after the electron irradiation, while they were formed near the electron incident surface with incubation times of several minutes in Fz–Si specimens.[4-7]) It is found that oxygen clusters are associated with the electron irradia-

Table 1 Comparison of fission neutron irradiation–induced defect densities of Cz–Si and Fz–Si between different temperature control mode at 673K.

	Cz–Si	Fz–Si
improved temp. control	$3.4x10^{13}/cc$	$2.3x10^{14}/cc$
convent. temp. control	$5.0x10^{13}/cc$	$4.5x10^{14}/cc$

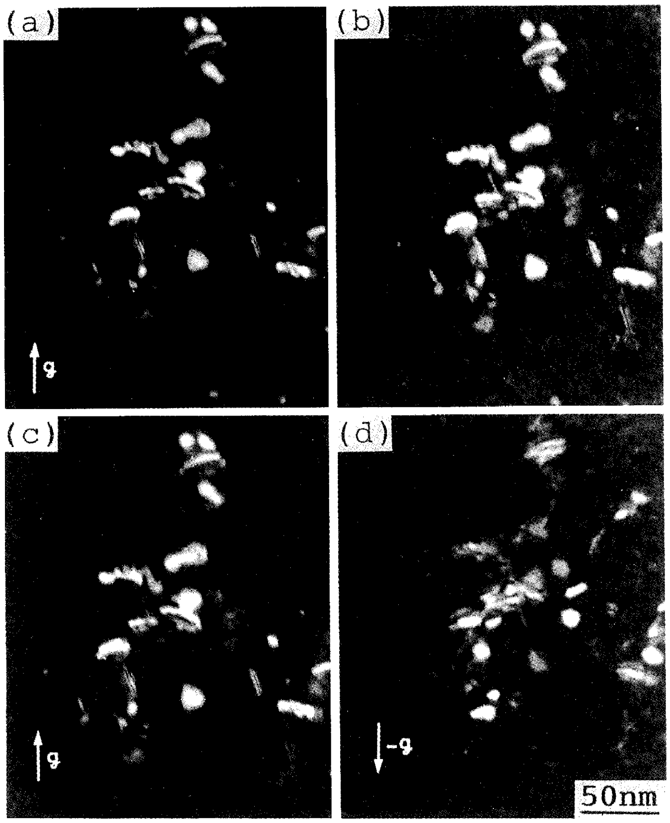
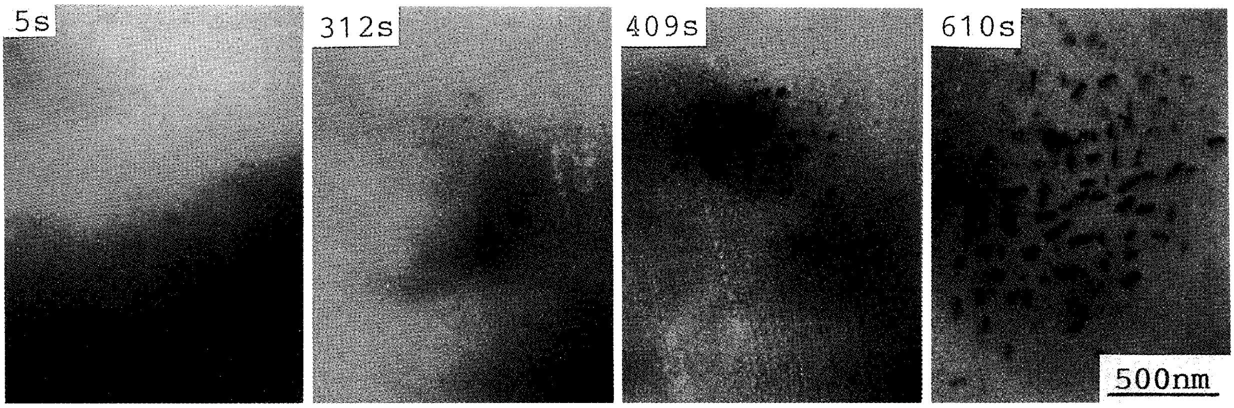
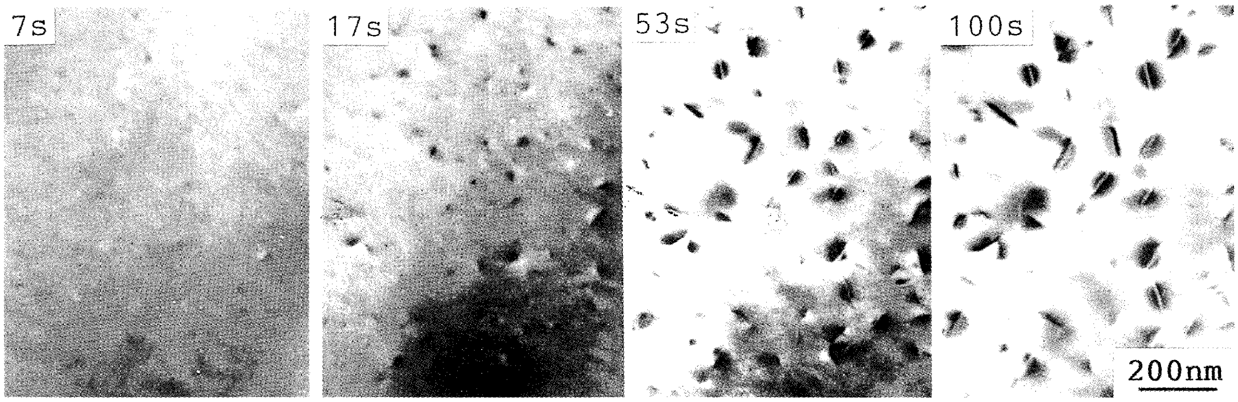


Fig.3 Determination of the nature of defects of Cz–Si irradiated at 673K with fission neutrons of JMTR with the fluence of $9.2x10^{19}n/cm^2$ by the inside–outside method; (a),(b) stereo pair, (c),(d) inside–outside pair



(a) Specimen: Pre-irradiated Cz-Si with fission neutrons of JMTR at 673K at the fluence of $9.0 \times 10^{19} n/cm^2$.
Electron dose: $1.6 \times 10^{19} e/cm^2$.



(b) Specimen: As-grown Cz-Si. Electron dose: $7.0 \times 10^{19} e/cm^2$.

Fig.4 Comparison of 2MeV electron irradiation effect at 673K between neutron pre-irradiated and un-irradiated Cz-Si. Insets indicate elapsed time of electron irradiation. In (a) nucleation of electron irradiation-induced defects is suppressed.

tion induced secondary defects. Comparison of electron irradiation effect between irradiated and un-irradiated Cz-Si with neutrons is shown in Fig.4(a) and (b). In the present experiments it was found that the electron irradiation-induced defect nucleation of Cz-Si specimens was suppressed markedly by neutron irradiation, suggesting that the state of interstitial oxygen atoms is changed during the neutron irradiation.

(3)JOYO, 683-703K, $1.8\text{-}6.4 \times 10^{22} n/cm^2$

Very complex defect clusters were formed, independent upon the type of specimen of Fz-Si and Cz-Si. It is seen that defect clusters were formed uniformly in the whole region of the specimen as shown in Fig.5. Characteristic diffraction effect with streaks and extra diffraction spots was also seen in the selected area diffraction patterns, but no indication of amorphous was obtained. In those specimens Kikuchi patterns were not observed, indicating that the lattice perfection became poor. In order to examine the origin of the extra spots and streaks, a parallel beam illumination method was used.[8] Although a long exposure time is needed, the size of diffraction spots becomes small and detailed shape analysis of the diffraction spots are possible by this technique. An example is shown in Fig.6. The selected area diffraction pattern taken from [011] pole shows a variety of diffuse scattering and streaks. Intense streaks lying along <111> directions strongly suggest the existence of {111} planar faults. Since this type of streaks was not found in electron irradiation induced secondary defects, the {111} stacking was disturbed markedly by heavy irradiation with neutrons. Most diffuse scattering is explainable due to intersections of the streaks along <113> and the Ewald sphere.

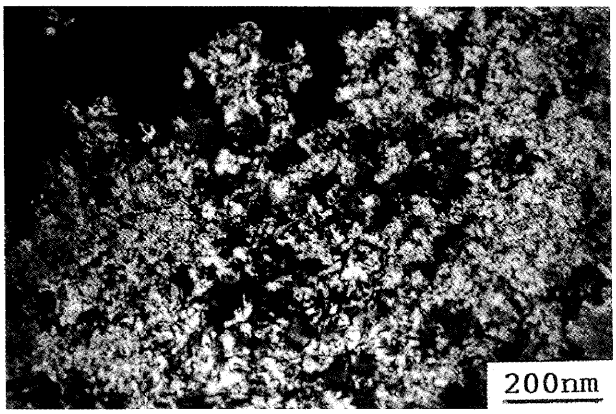


Fig.5 Dark field electron micrograph of defect clusters of Si irradiated with fission neutrons of JOYO at the fluence of $2.5 \times 10^{22} n/cm^2$ at 703K.

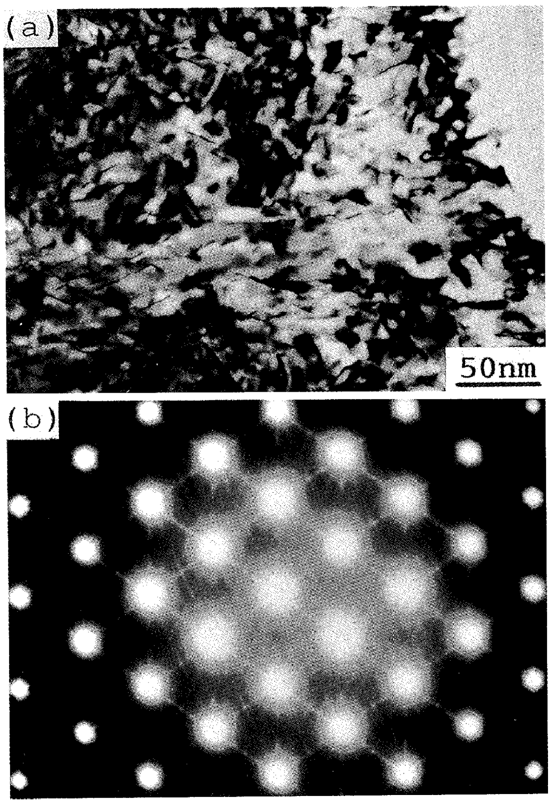


Fig.6 TEM image of microdefects (a) and the selected area diffraction pattern with 110 orientation (b) showing streaks and diffuse scattering.

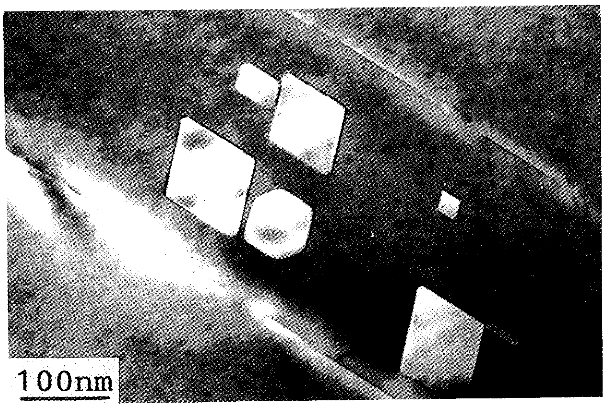


Fig.7 Precipitates formed in Si irradiated with fission neutrons of JOYO at the fluence of $7.2x10^{22}n/cm^2$ at 1043K.

(4)JOYO, 1043K, $7.2x10^{22}n/cm^2$

Since the irradiation temperature was so high that neutron irradiation-induced defects were annihilated, remarkable secondary defects were not observed. Only dislocation loops and precipitates were observed as shown in Fig.7.

(5)Computer simulation

It is reported that the displaced threshold energy of silicon is 15.8eV which is not much dependent on the incident beam direction.[9] The mean free path of scattering of incident neutrons, L is calculated by $L=1/N{\cdot}s$, where $N=5x10^{22}/cm^3$ is the density of atoms of silicon and $s=3x10^{-24}cm^2/atom$ is the reaction cross section for 1.5MeV neutrons, and L=6.7cm is obtained. This means that a neutron collided with a silicon atom once is scattered to outside of the TEM specimen. The PKA energy was calculated with a cross section of neutrons for elastic scattering for silicon.[2] The maximum and averaged PKA energies are obtained to be 200keV and 100keV, respectively.

Marlowe code computer simulation shows that a cascade structure is formed with a vacancy rich region in the center and an interstitial rich region surrounding it. An example is shown in Fig.8 for the case of the PKA energy of 100keV. The size of a cascade slightly depends on the PKA energies, but has an order of $10nm^3$. The vacancy and interstitial cluster sizes obtained by the computer simulation are presented in Fig.9. It is found that vacancies are present as multi-vacancy clusters, while interstitial atoms are rather isolated.

4. Discussion

Although most irradiation work on silicon indicate that interstitial type secondary defects are formed, the present neutron irradiation at 473K shows the formation of vacancy type defect clusters of several nanometers, the size of which is corresponding to the vacancy rich regions obtained by the computer simulation. Same type defect clusters were already reported in the fusion neutron irradiated silicon.[10] The present results suggest that the defect clusters were directly formed by collapse of vacancy rich regions of

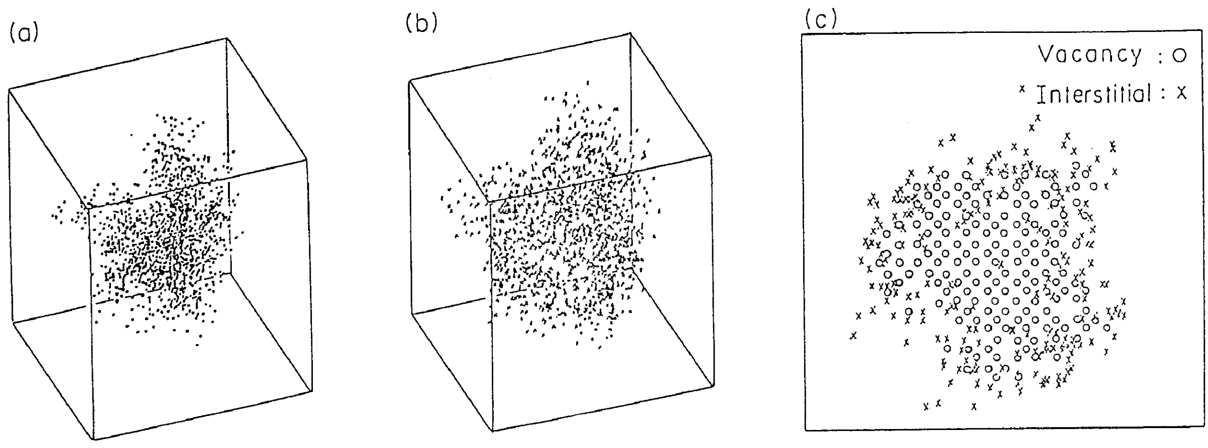


Fig.8 Simulated distribution of defects in a cascade, in which the PKA energy of 100keV is given at the central atom along [111]. The edge length is 5.6nm. (a) vacancies, (b) interstitials and (c) a cross section illustration of (a) and (b).

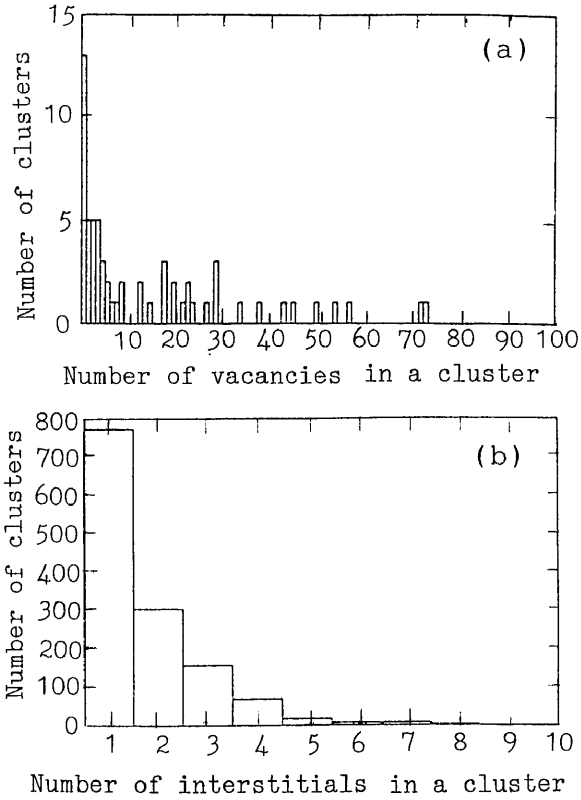


Fig.9 Number density of vacancy clusters (a) and interstitial clusters (b) in a cascade obtained by Marlowe code computer simulation, in which the PKA energy of a Si atom along [110] is 200keV.

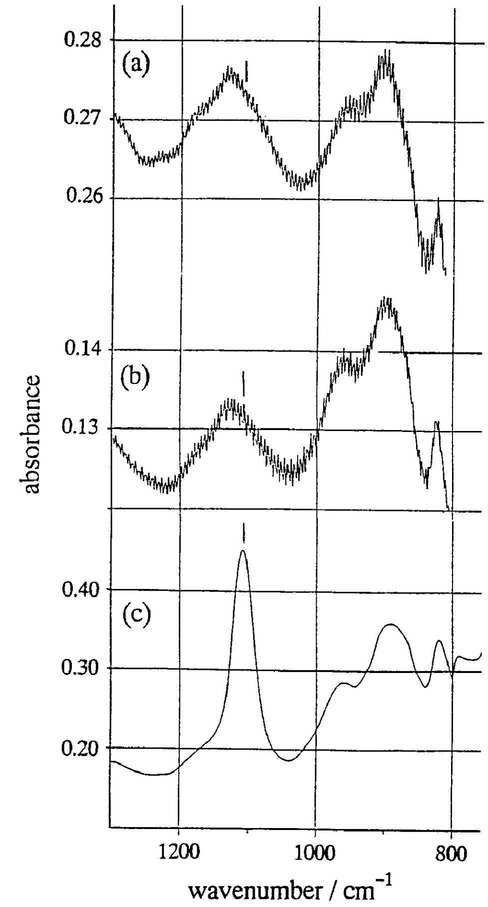


Fig.10 Micro-FT-IR spectra of Si irradiated with fission neutrons of JOYO at the fluence of 2.5x10^{22}n/cm^2 at 703K: (a) and (b) irradiated samples, and (c) un-irradiated Cz-Si as a reference.

cascades. However, the density was two orders magnitude lower than that of the calculation, showing that the number of cascades was decreased to a considerable extent presumably by mutual annihilation of interstitials and vacancies during irradiation. Taking into account that the multi-vacancies were immobile at 473K, it is concluded that the vacancy type defect clusters are associated with them. On the other hand, defect clusters formed by irradiation at temperatures around 673K were interstitial type, and they made colonies with a size larger than 500 nanometers. In this case, the initial cascade structures were no longer retained, and such large damage structure formation is considered to be associated with aggregation of free interstitials diffused out from the cascades. Another notable fact in the present experiment is that the state of interstitial oxygen atoms may be changed by neutron irradiation. The micro FT-IR measurements clearly showed that the concentration of interstitial oxygen was decreased to an order of 10^{17}/cc for all of the irradiated specimens examined by transmission electron microscopy. As shown in Fig.10, no indication of interstitial oxygen atoms at 1107cm^{-1} was found in the irradiated samples(a,b) though the signal to noise ratio was poor because of thinness of the samples. This fact clearly shows that the content of interstitial oxygen atoms is decreased to an undetectable level by the micro-FT-IR.

Acknowledgment

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